



OFFICE OF NAVAL RESEARCH

Grant N00014-91-J-1043

R & T code 4135014

Technical Report No. 3

Synthesis and X-Ray Structure of a Zirconacyclopropene-Alkyne Complex: On The Mechanism of Zirconium-Mediated Reductive Coupling of Alkynes

by

Benjamin P. Warner, William M. Davis, and Stephen L. Buchwald

Prepared for Publication  
in the  
*Journal of the American Chemical Society*

Massachusetts Institute of Technology  
Department of Chemistry  
Cambridge, MA 02139

May 27, 1993

Accession For	
NTIS	CRA&I <input checked="" type="checkbox"/>
DTIC	TAB <input checked="" type="checkbox"/>
Unannounced <input checked="" type="checkbox"/>	
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale, its distribution is unlimited.

**Synthesis and X-ray Structure of a Zirconacyclopropene-Alkyne Complex: On the Mechanism of Zirconium-Mediated Reductive Coupling of Alkynes**

Benjamin P. Warner, William M. Davis, and Stephen L. Buchwald\*

*Department of Chemistry*

*Massachusetts Institute of Technology*

*Cambridge, Massachusetts 02139*

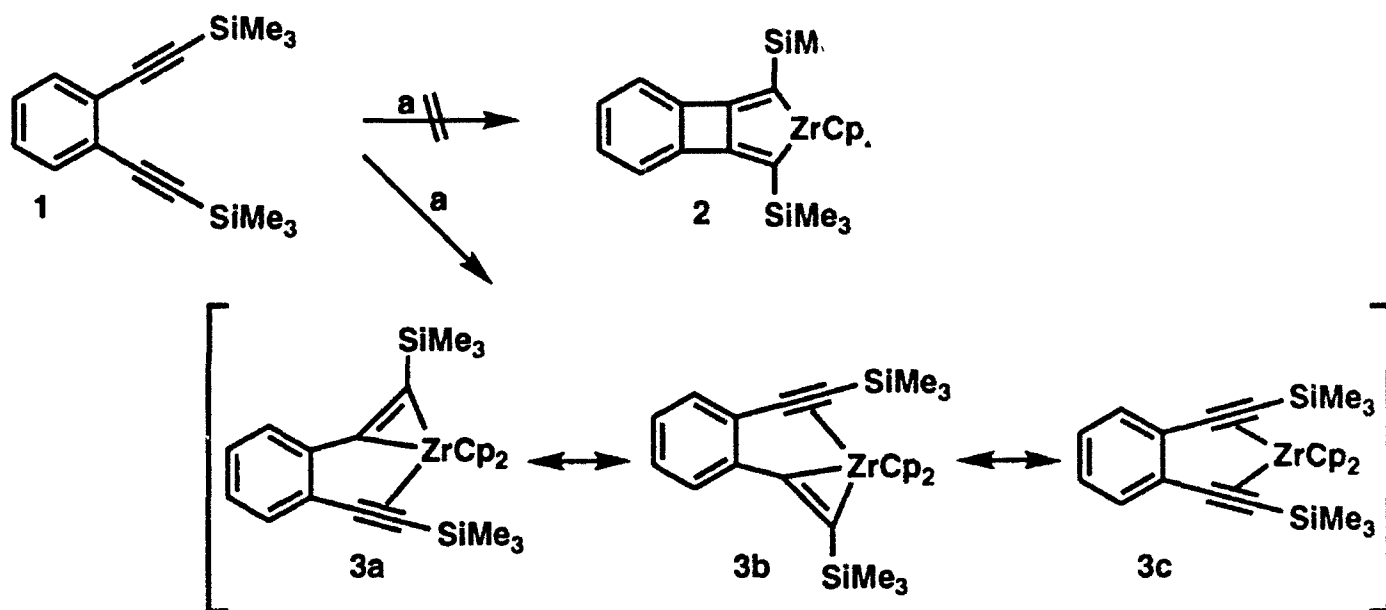
**ABSTRACT**

The zirconocene-mediated reductive coupling of alkynes has been proposed to proceed *via* an intermediate zirconacyclopropene-alkyne (bis-alkyne) complex. Herein, we report the first preparation and X-ray crystal structure determination of such a zirconacyclopropene-alkyne (bis-alkyne) complex.

For several years we have been interested in the synthesis and the study of the structural properties of main group metallacycles<sup>1</sup>. These species are often available *via* transmetalation of a zirconacycle precursor<sup>2</sup>. Molecular structure appear to have superior packing properties in "zirconacycle 2 would be a useful precursor to 1". Treatment of 1<sup>3</sup> (Scheme I) with an equivalent of agent<sup>4</sup>, unexpectedly failed to give 2<sup>4,5</sup>, and instead orange crystals<sup>6</sup>.

*Technical Report*

**Scheme I**



a.  $\text{Cp}_2\text{ZrCl}_2/2 \text{ nBuLi/THF/-78}^\circ \text{C to RT, then hexane to } 70^\circ \text{C (55\%)}$

[Figure 1]

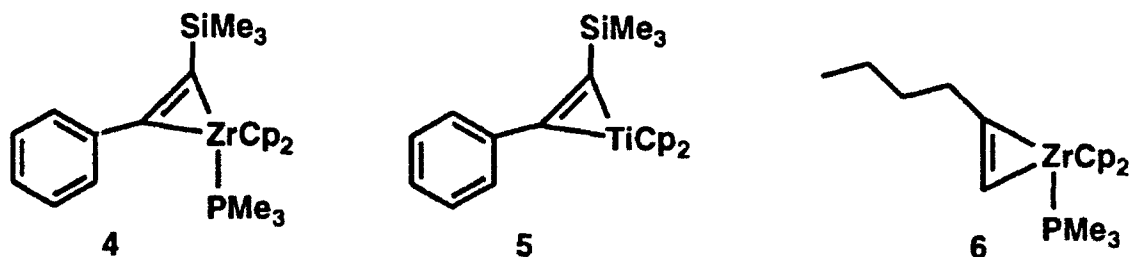
The three most plausible resonance structures for **3** are shown in Scheme I. Both the spectroscopic and crystallographic data which we have collected indicate that **3a** and **3b** are the major resonance forms, and that **3c** is a minor contributor.<sup>7</sup> Consistent with this representation, no change, other than slight broadening, is observed in the  $^1\text{H}$  NMR spectrum at temperatures as low as  $-92^\circ \text{C}$  (toluene- $d_8$ ). The IR spectrum exhibits only a single stretch in the alkyne region at  $1816 \text{ cm}^{-1}$ . This signal is approximately mid-way between that observed for **1** at  $2161 \text{ cm}^{-1}$ , and that seen in normal group 4 metallocene complexes of

alkynes (metallacyclopropenes) in **4**<sup>8</sup> at 1620 cm<sup>-1</sup> and **5**<sup>9</sup> at 1686 cm<sup>-1</sup>. Similarly, in the <sup>13</sup>C NMR spectrum of **3**, signals for only two alkynyl carbons are present at 143.3 and 154.2 ppm. These resonances are roughly equidistant from those observed for their counterparts in **1** (98.4 and 103.3 ppm), and **4** (177.4 and 181.0 ppm) and **5** (213.0 and 219.6 ppm). An ORTEP of the structure resulting from an X-ray diffraction determination is shown in Figure 1. The effects of  $\pi$ -backbonding are manifested by the fact that the C1-C2 bond distance of 1.258(5) Å in **3** is substantially longer than the value of 1.195(3) Å seen in hexakis(trimethylsilylethynyl)benzene<sup>10</sup>. This longer bond length is close to that displayed by other zirconacyclopropenes, such as **6**<sup>11a</sup>, in which the corresponding carbon-carbon bond length is 1.286(5) Å. Further, in **3** the C2-C1-Si and C1-C2-C3 bond angles are similar to the analogous angles in **4**, **5** and **6** (Table 1). Taken together, the spectroscopic and crystallographic data both support the conclusion that **3** is best described as a zirconacyclopropene-alkyne complex.

Table 1: Comparison of selected bond angles of compounds **3-6**.

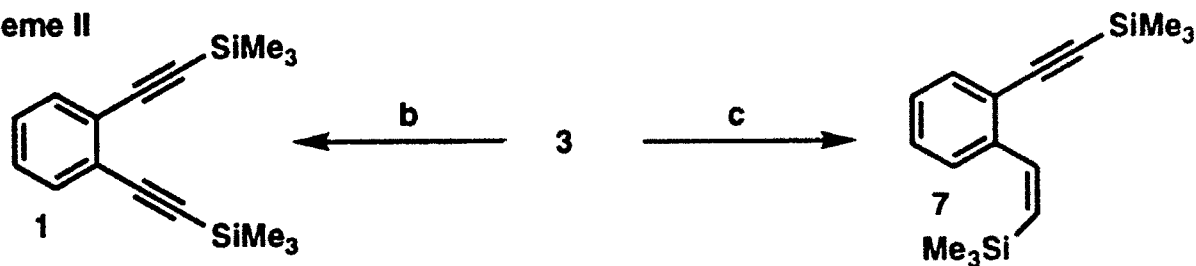
Compound	C2-C1-Si bond angles °	C1-C2-C3 bond angles °
<b>3</b>	140.2(3)	154.8(4)
<b>4</b>	148.2(2)	141.0(2)
<b>5</b>	140.8(3)	151.9(3)
<b>6</b>	--	135.8(3)

Figure 2



The reactions of **3** are also consistent with the above structural description (Scheme II).

Scheme II

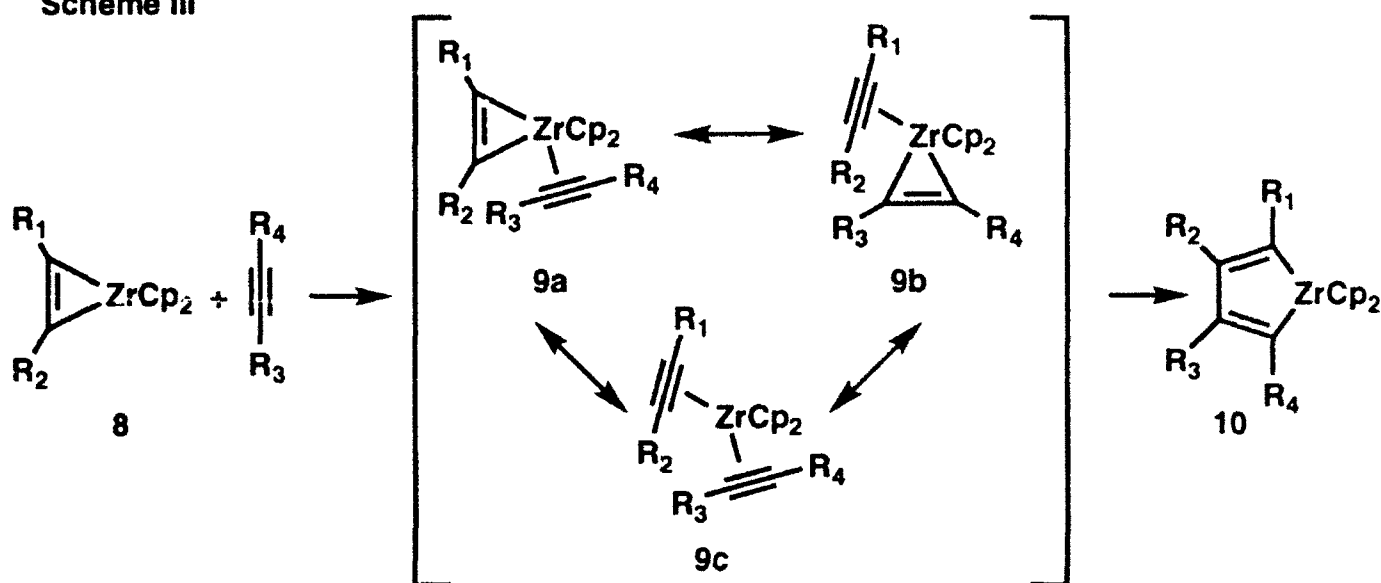


**b.** I<sub>2</sub>/THF/-78° C (88%) **c.** H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/THF (92%)

For example, treatment of **3** with I<sub>2</sub> produces zirconocene diiodide and reforms **1** in 88% yield<sup>12</sup>. Treatment of **3** with aqueous sulfuric acid gives enyne **7**, in 92% yield<sup>5a,12</sup>. This result is similar to that seen by Nugent, where hydrolysis of the product of the reaction of "titanocene" and 2,6-octadiyne yielded *Z*-6-octene-2-yne<sup>5a</sup>.

Group 4 metallocene-induced reductive coupling of alkynes have been proposed to proceed as shown in scheme III<sup>5a,13</sup>. The zirconocene-alkyne complex **8**, best described as a zirconacyclopropene<sup>5a,11,13b</sup>, reacts with a second alkyne to form **9a (9b)**<sup>5a,13</sup>, an 18 electron intermediate which has also been described as a bis-alkyne complex **9c**<sup>5a,13a</sup>. Insertion of the alkyne into the zirconium-carbon bond produces a zirconacyclopentadiene **10**. Other metal-mediated reductive coupling reactions have been proposed to proceed via similar mechanisms<sup>14</sup>, and some intermediate species have been isolated<sup>14b-d</sup>. While several examples of zirconacyclopropenes<sup>11</sup> and zirconacyclopentadienes<sup>5a,13a</sup> have been isolated and structurally characterized, complex **3** represents, to our knowledge, the first example of the intermediate zirconacyclopropene-alkyne (bis-alkyne) complex.

**Scheme III**



In summary, we have isolated and structurally characterized a zirconacyclopentadiene-alkyne complex. Treatment of **1** with zirconocene-butene does not proceed to the zirconacyclopentadiene, but instead yields **3**. This demonstrates, for the first time, the viability of such a complex, which has been proposed as an intermediate in the zirconocene-induced reductive coupling of alkynes. We are continuing to examine the factors that affect these cyclizations, and their use in the synthesis of main group metallacycles with interesting physical properties.

**Acknowledgment.** We thank the Office of Naval Research for partial support of this research. SLB acknowledges additional support received as an Alfred P. Sloan Fellow (1988-92) and a Camille & Henry Dreyfus Teacher-Scholar. We thank Dr. William Nugent for helpful discussions.

**Supplementary Material Available:** Full experimental procedures for the preparation of **3** and **7**. NMR, IR, and elemental analysis or HRMS characterization of compounds **3** and **7**, along with the crystallographic data and procedures, an ORTEP diagram of **3**, tables of bond distances and angles for **3**, and a table of final positional and thermal parameters for **3** (25

pages); table of structural factors for **3** (9 pages). Ordering information is given on any current masthead page.

#### Footnotes:

- (1) (a) Buchwald, S.L.; Fisher, R.A.; Foxman, B.M. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 771. (b) Buchwald, S.L.; Fisher, R.A.; Davis, W.M. *Organometallics* **1989**, *8*, 2082. (c) Fisher, R.A.; Nielsen, R.B.; Davis, W.M.; Buchwald, S.L. *J. Am. Chem. Soc.* **1991**, *113*, 165. (d) Spence, R.E.V.H.; Hsu, D.P.; Buchwald, S.L. *Organometallics* **1992**, *11*, 3492.
- (2) Fagan, P.J.; Nugent, W.A. *J. Am. Chem. Soc.* **1988**, *110*, 2310.
- (3) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis*, **1980**, 627.
- (4) (a) Negishi, E.; Cederbaum, F.E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (b) Binger, P.; Muller, P.; Benn, R.; Rufinska, A.; Gabor, B.; Kruger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 1035.
- (5) (a) Nugent, W.A.; Thorn, D.L.; Harlow, R.L. *J. Am. Chem. Soc.* **1987**, *109*, 2788. (b) Buchwald, S.L.; Nielsen, R.B. *J. Am. Chem. Soc.* **1989**, *111*, 2870. (c) Thanedar, S.; Farona, M.F. *J. Organomet. Chem.* **1982**, *235*, 65. (d) Yoshifuji, M.; Gell, K.I.; Schwartz, J. *J. Organomet. Chem.* **1978**, *153*, C15. (e) A cobalt-mediated cyclization of **1** has been performed as part of a synthesis of biphenylenes, see Berris, B.C.; Hovakeemian, G.H.; Lai, Y.H.; Mestdagh, H.; Vollhardt, K.P.C. *J. Am. Chem. Soc.* **1985**, *107*, 5670.
- (6) The initial reaction mixture also includes (as determined by  $^1\text{H}$  NMR) the symmetrical zirconacyclopentadiene formed by coupling two equivalents of **1**. Upon heating the reaction products in hexane, this disproportionates into **1** and **3**. See Gesing, E.R.F. *J. Chem. Soc., Chem. Commun.* **1982**, 426.
- (7) For a cogent discussion on the related question of whether metallacyclopropanes and metal-olefin complexes are resonance forms, cf: Bender, B.R.; Norton, J.R.; Miller, M.M.; Anderson, O.P.; Rappe, A.K. *Organometallics* **1992**, *11*, 3434.
- (8) Erker, G.; Zwettier, R. *J. Organomet. Chem.* **1991**, *409*, 179.



- (9) Rosenthal, U.; Gorls, H.; Burlakov, V.V.; Shur, V.B.; Vol'pin, M.E. *J. Organomet. Chem.* **1992**, 426, C53.
- (10) Diercks, R.; Armstrong, J.C.; Boese, R.; Vollhardt, K.P.C. *Angew. Chem. Int. Ed. Engl.* **1986**, 25, 268.
- (11) (a) Buchwald, S.L.; Watson, B.T. *J. Am. Chem. Soc.* **1987**, 109, 2544. (b) Buchwald, S.L.; Lum, R.T.; Dewan, J.C. *J. Am. Chem. Soc.* **1986**, 108, 7441. (c) Buchwald, S.L.; Watson, B.T.; Huffman, J.C. *J. Am. Chem. Soc.* **1986**, 108, 7411.
- (12) Takagi, K.; Rousset, C.J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, 113, 1440.
- (13) This mechanistic proposal was first suggested, to our knowledge, by Nugent, et al.<sup>5a</sup> For closely related mechanistic descriptions, cf: (a) Erker, G.; Zwettler, R.; Kruger, C.; Hyla-Kryspin, I.; Gleiter, R. *Organometallics*. **1990**, 9, 524. (b) Buchwald, S.L.; Neilsen, R.B. *Chem. Rev.* **1988**, 88, 1047 and references therein. (c) Yasuda, H.; Nakamura, A. *Angew. Chem. Int. Ed. Engl.* **1987**, 26, 723. Similar associative mechanisms for alkyne-olefin coupling reactions are proposed in: (d) Negishi, E.; Holmes, S.J.; Tour, J.M.; Miller, J.A.; Cederbaum, F.E.; Swanson, D.R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, 111, 3336. (e) Tidwell, J.H.; Senn, D.R.; Buchwald, S.L. *J. Am. Chem. Soc.* **1991**, 113, 4685.
- (14) (a) Wakatsuki, Y.; Nomura, O.; Kituara, K.; Morokuma, K.; Yamakazi, H. *J. Am. Chem. Soc.* **1983**, 105, 1907. (b) Yamakazi, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, 139, 157. (c) Yamakazi, H.; Hagihara, N. *J. Organomet. Chem.* **1967**, 7, P22. (d) Weillstra, Y.; Gambarotta, S.; Meetsma, A.; de Boer, J.L.; *Organometallics* **1989**, 8, 2696.

Figure 1. ORTEP diagram of **3** with selected bond distances and angles. Selected Bond Distances (Å): Zr1-C1, 2.346(4); Zr1-C2, 2.390(4); Si1-C1, 1.854(4); C1-C2, 1.255(5); C2-C2', 2.319(7); C2-C3, 1.460(5). Selected Bond Angles (°): Si1-C1-C2, 140.0(3); C1-C2-C3, 55.2(4); C2-C3-C3', 108.9(2); Zr1-C1-C2, 76.6(2); Zr1-C2-C1, 72.7(2); C1-Zr1-C2, 30.7(1). Primed atoms are at -x, y, 1/2-z.

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)\*  
Chemistry Division, Code 1113  
800 North Quincy Street  
Arlington, Virginia 22217-5000

Dr. James S. Murday (1)  
Chemistry Division, Code 6100  
Naval Research Laboratory  
Washington, D.C. 20375-5000

Dr. Robert Green, Director (1)  
Chemistry Division, Code 385  
Naval Air Weapons Center  
Weapons Division  
China Lake, CA 93555-6001

Dr. Elek Lindner (1)  
Naval Command, Control and Ocean  
Surveillance Center  
RDT&E Division  
San Diego, CA 92152-5000

Dr. Bernard E. Douda (1)  
Crane Division  
Naval Surface Warfare Center  
Crane, Indiana 47522-5000

Dr. Richard W. Drisko (1)  
Naval Civil Engineering  
Laboratory  
Code L52  
Port Hueneme, CA 93043

Dr. Harold H. Singerman (1)  
Naval Surface Warfare Center  
Carderock Division Detachment  
Annapolis, MD 21402-1198

Dr. Eugene C. Fischer (1)  
Code 2840  
Naval Surface Warfare Center  
Carderock Division Detachment  
Annapolis, MD 21402-1198

Defense Technical Information  
Center (2)  
Building 5, Cameron Station  
Alexandria, VA 22314

\* Number of copies to forward